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EVOLVED GAS ANALYSIS AT THERMAL TREATMENT OF SOME SOLID FOSSIL FUELS

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Coupled TG-FTIR technique was used for identification of gaseous compounds evolved at thermal treatment of six coal samples from different deposits (Bulgaria, Russia, Ukraine). The experiments were carried out under dynamic heating conditions up to 900°C at heating rates of 5, 10 or 50 K min^{-1} in a stream of dry air. The emission of CO_2, H_2O, CO, SO_2, COS, methane, methanol, formic acid, formaldehyde, acetaldehyde, chlorobenzene was clearly identified in FTIR spectra of the samples studied. The formation of ethanol, ethane, ethylene and *p*-xylene, at least on the level of traces, was also identified. At the heating rate of 5°C min^{-1} the temperature of maximum intensities of the characteristic peaks of COS was 270°C, of formaldehyde, formic acid, ethane and methanol 330°C, of SO_2, CO, acetic acid, ethylene and *p*-xylene 400°C and of chlorobenzene 500°C. At 10°C min^{-1} and 50°C min^{-1} these temperatures were shifted, respectively, by 70–300°C and 150–450°C towards higher temperatures and the respective absorption bands in FTIR spectra were, as a rule, more intensive.

Keywords: *coal, EGA, TG-FTIR, thermal treatment*

Introduction

The use of coupled TG-FTIR technique for characterization of solid fossil fuels enables qualitative identification of gaseous compounds evolved at thermal treatment of samples in neutral [1–3] as well as in oxidative [4, 5] medium and to explain more precisely the changes observed on thermogravimetric curves. Earlier, the results of thermal treatment of different oil shale samples using TG-FTIR equipment were presented in [6]. The goal of the present study was the thermal characterization of six coal samples from different deposits (Bulgaria, Russia, Ukraine).

Experimental

Materials

Three samples of Bulgarian (B), two samples of Russian (R) and one sample of Ukrainian (U) coal were studied (Table 1). The samples were prepared according to ASTM standard D2013-03. Elemental composition of the samples was determined with a Vario EL analyzer and the gross calorific value with a calorimeter B-08BM. For element analysis the previously air-dried and ground samples were supplementary dried at 105°C for 24 h.

Methods

The coupled TG-FTIR system used consisted of Setaram Labsys 2000 equipment interfaced to an Interspec 2020 Fourier Transform Infrared Spectrometer as described precisely in [6]. FTIR measurements were recorded in the 4000–600 cm^{-1} region with a resolution of 4 cm^{-1} and as an average of 4 scans. The Bio-Rad (Sadtler) KnowItAll search program and Gases&Vapours Database (code GS) and Organics and Polymers Database (code TU, SR) were used.

The experiments were carried out under dynamic heating conditions up to 900°C at heating rates of 5, 10 or 50 K min^{-1} in a stream of dry air (70 mL min^{-1}). In the case of 50°C min^{-1} heating rate the final temperature was held constant during 15 min. Standard 100 μL Pt-crucibles were used and the mass of samples was 16–20 mg.

Results and discussion

Thermal analysis

At the heating rates of 5 and 10°C min^{-1} the emission of absorbed water and gaseous species proceeded up to 150–180°C and the mass loss at that was in the range of 2–10% being the highest for B5 (Fig. 1). At the heating rate of 50°C min^{-1} it continued up to 200–230°C with the mass loss of 1–8.5% (Fig. 2).

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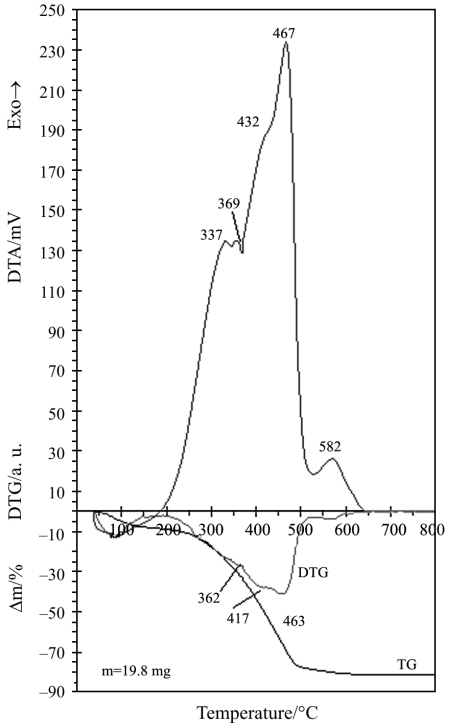

Fig. 1 Thermoanalytical curves of Bulgarian coal 5 at the heating rate of 5°C min^{-1}

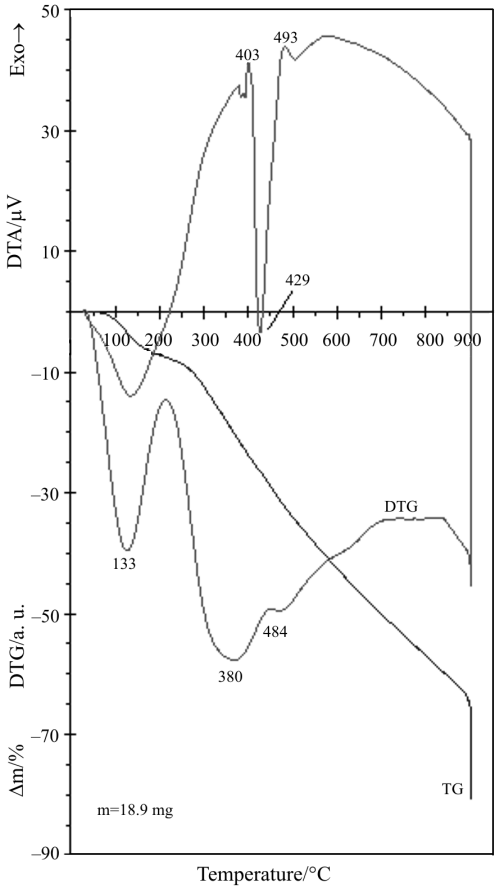

Fig. 2 Thermoanalytical curves of Bulgarian coal 5 at the heating rate of 50°C min^{-1}

The thermooxidation of organic matter in the DTA curve proceeded roughly in two steps, the first one corresponds to the thermooxidation of lighter part of volatile matter and the second one to thermooxidation of heavier part of volatile matter and fixed carbon [4, 6, 7] as well as to thermooxidation of pyrite [8, 9]. At the heating rates of 5 and 10°C min^{-1} the first step lasted, depending on the origin of the sample, up to 300–380°C being the lowest for B2 and the highest for R13. The second step continued up to 550°C (B2) or 750°C (U9), the total mass loss considering both steps of thermooxidation was 60–88%.

At the heating rate of 50°C min^{-1} the peak maxima in DTA and DTG curves as well as the boundary between the first and second step were shifted by 30–50°C towards higher temperatures as compared to low heating rates. This phenomena is in a good correlation with the results published earlier [5, 6, 10]. The maxima of exoeffects in DTA curves at 371 and 470° for B3 and at 403 and 493° for B5 are very clearly separated by a deep minimum between them at 397 and 429°C, respectively (Fig. 2). It could be explained by a higher content of volatile matter (higher ratio of H/C) in Bulgarian coal as compared to Russian and Ukrainian coal samples (Table 1) which evolved very intensively (explosively) at the fast heating rate. For these samples, especially, for R12 and R13, the exoeffect in the DTA curve was presented only as one big

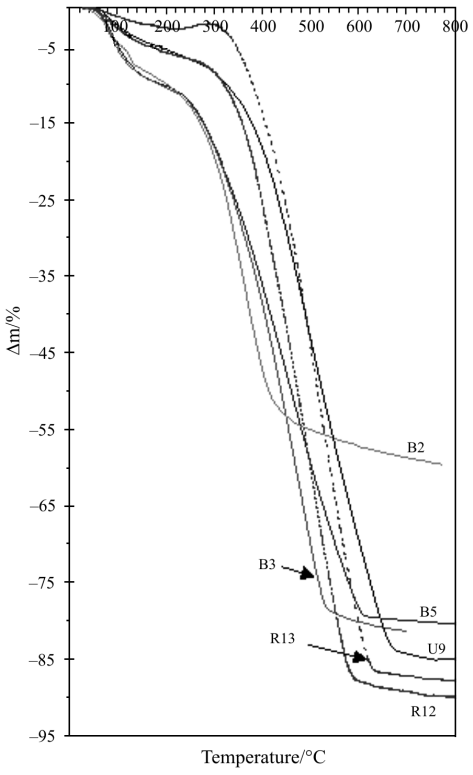

Fig. 3a TG curves of samples thermooxidated at the heating rate of 10°C min^{-1}

Table 1 Main characteristics of samples (on dry bases)

Content/%	Sample					
	B2 (tailings)	B3	B5	U9	R12	R13
Volatile matter	35.1	50.1	50.4	33.8	37.6	37.1
Ash	40.2	17.8	17.2	14.0	11.5	11.0
$(CO_2)_M$	0.4	0.1	0	1.3	0	0.1
S_{total}	4.42	5.86	5.69	1.01	3.29	2.48
S_{pyr}	1.13	2.41	1.66	0.46	0	0.01
S_{sulph}	1.43	0.26	0.27	0.13	0.66	0.18
S_{org}	1.86	3.19	3.76	0.42	2.63	2.29
N	0.47	0.60	0.59	1.06	1.37	1.45
H	3.37	5.00	5.20	4.07	5.15	5.05
C	34.87	54.15	54.59	62.86	67.71	75.98
H/C	0.097	0.092	0.095	0.065	0.076	0.066
Gross calorific value/MJ kg^{-1}	16.80	23.18	23.09	27.64	29.82	32.10

massive with mini maximums and shoulders. The mass loss was completed after two (B2) to nine (R13) minutes of holding the samples at 900°C (Fig. 3b). The total mass loss was 1–3% smaller than at the lower heating rates (Figs 1–3) that could be caused by the incomplete changes within the mineral part of samples or partial binding of species (SO_2, HCl) formed and evolved during thermooxidation of the samples.

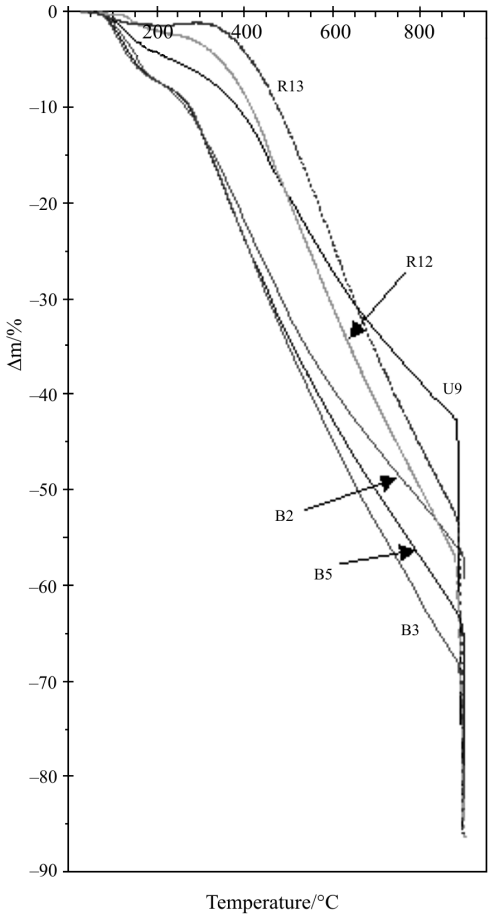

Fig. 3b TG curves of samples thermooxidated at the heating rate of 50°C min^{-1}

FTIR analysis

The list of gaseous compounds evolved at thermooxidation of coal samples studied was in a good correlation with the results described in [4–6].

In addition to CO_2 (characteristic peaks at 2380 and 721 cm^{-1}) and water (absorption bands in broad ranges 3900–3500 and 1900–1300 cm^{-1}) as main species evolved, there were clearly fixed the characteristic peaks for methane (3016 and 1307 cm^{-1}), CO (2178 and 2113 cm^{-1}), acetic (1798 and 1176 cm^{-1}) and formic (1749 and 1108 cm^{-1}) acids, formaldehyde (1749 and 1706 cm^{-1}), ethylene (1648 and 950 cm^{-1}), SO_2 (1375 and 1362 cm^{-1}), *p*-xylene (1512 and 793 cm^{-1}), chlorobenzene (1473 and 742 cm^{-1}) and NH_3 (967 and 933 cm^{-1}) in FTIR spectra of all the samples studied.

At least on the level of traces, also the characteristic peaks for ethane (2970 and 1458 cm^{-1}), HCl (absorption bands in broad ranges 3000–2700 cm^{-1}), acetaldehyde (1763 and 1420 cm^{-1}), ethanol (1244 and 1052 cm^{-1}) and possibly furan (746 cm^{-1}) were identified in FTIR spectra (Figs 4–5).

The absorption bands characteristic to COS (2074 and 2052 cm^{-1}) and methanol (1060, 1034 and 1006 cm^{-1}) were clearly fixed in FTIR spectra of Bulgarian coal samples, for R13 these were of much lower intensity and for U9 and R12 on the level of traces (Figs 6 and 7).

B5 (like Bulgarian coal samples in general) has intensive characteristic peaks in FTIR spectra of

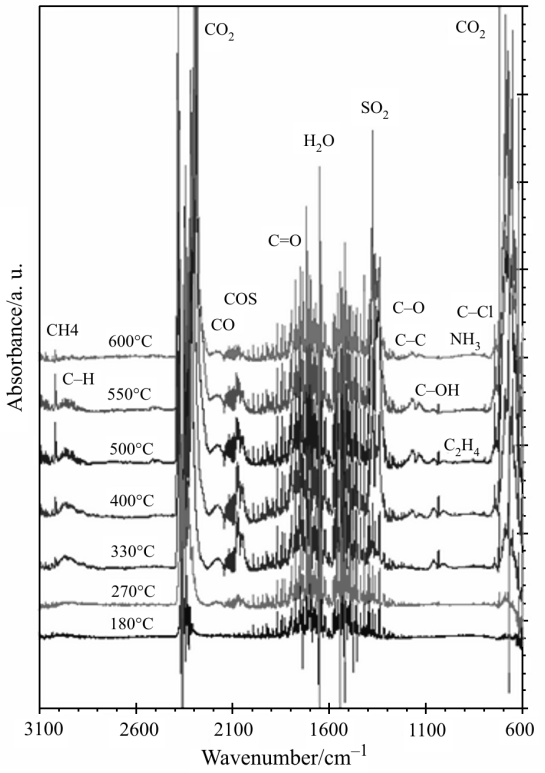

Fig. 4 FTIR spectra of gaseous compounds evolved at thermooxidation of Bulgarian coal 5 at the heating rate of 10°C min^{-1}

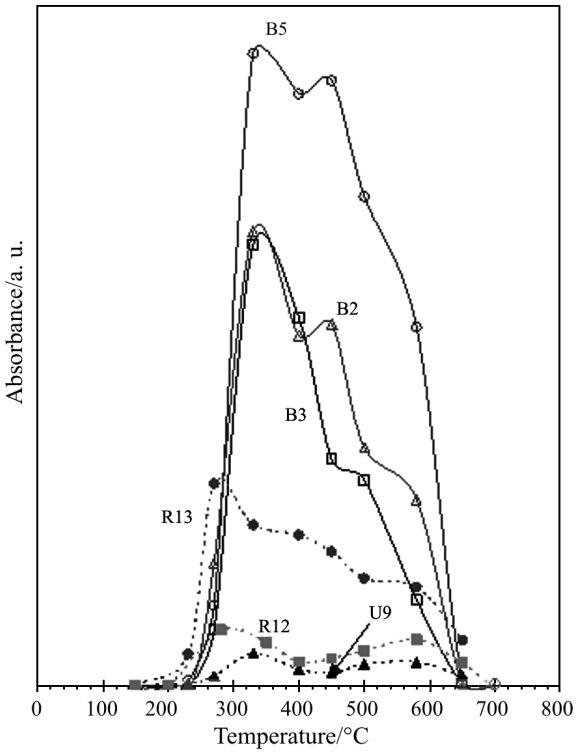

Fig. 6 Absorbance profiles of COS evolved at thermooxidation of coal samples at the heating rate of 10°C min^{-1}

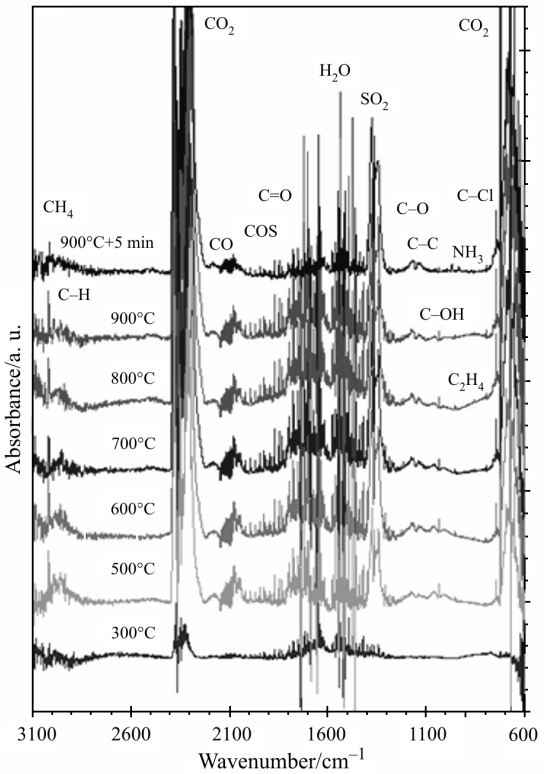

Fig. 5 FTIR spectra of gaseous compounds evolved at thermooxidation of Bulgarian coal 5 at the heating rate of 50°C min^{-1}

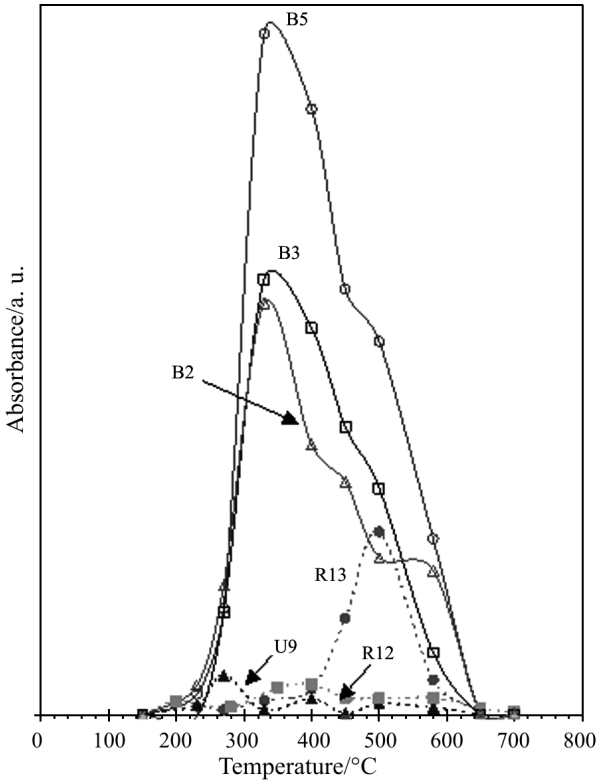

Fig. 7 Absorbance profiles of methanol evolved at thermooxidation of coal samples at the heating rate of 10°C min^{-1}

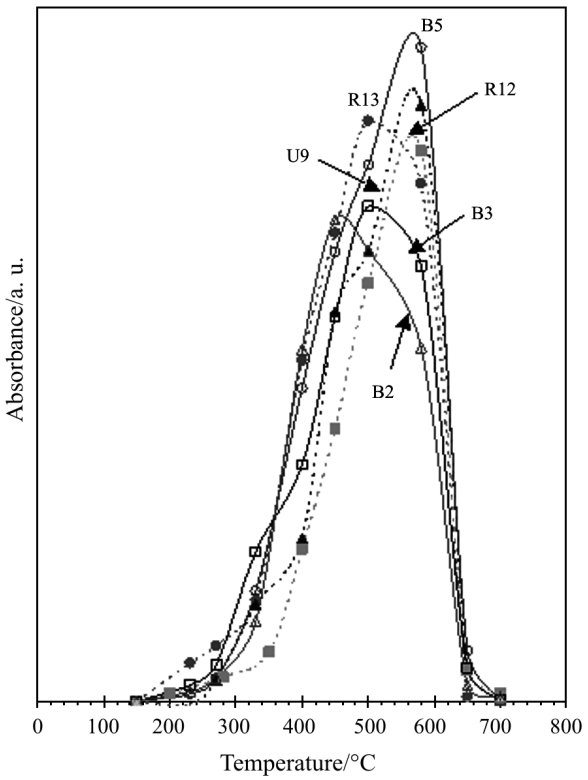

Fig. 8 Absorbance profiles of chlorobenzene evolved at thermooxidation of coal samples at the heating rate of 10°C min^{-1}

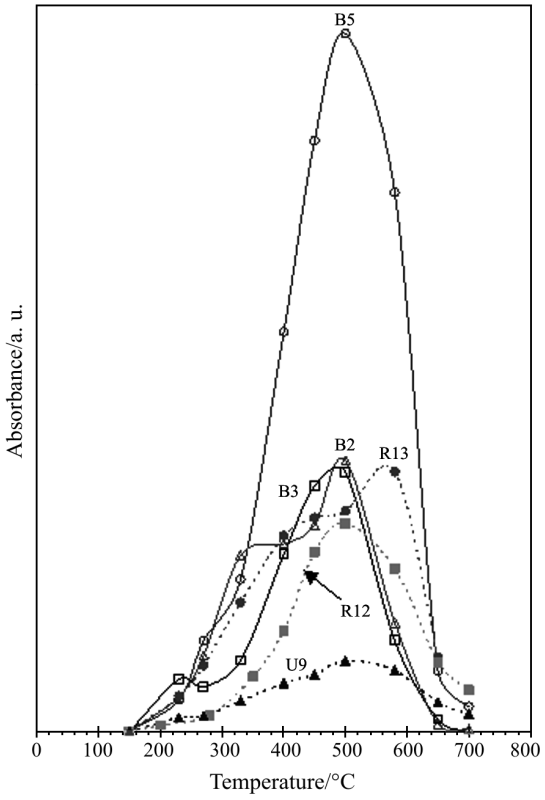

Fig. 9 Absorbance profiles of SO_2 evolved at thermooxidation of coal samples at the heating rate of 10°C min^{-1}

many organic compounds, for example, of COS, formaldehyde, methanol, chlorobenzene, *p*-xylene, etc. as well as of SO_2 (Figs 6–9). The intensive emission of organic compounds could be explained by high content of volatile matter (by the H/C ratio) and SO_2 emission by high content of organic and pyritic sulphur in B5 and in the other Bulgarian coal samples (Table 1). The absorption bands in FTIR spectra characteristic to NH_3 were more intensive for Russian and Ukrainian coal samples than for Bulgarian ones that is in a good correlation with the content of nitrogen in these samples (Table 1).

The beginning of emission of most gaseous compounds formed at thermooxidation of the samples studied at heating rates of 5 and 10°C min^{-1} was fixed in the interval of 180–250°C, but some of them like *p*-xylene and chlorobenzene at 250–300°C (Fig. 4).

At 5°C min^{-1} heating rate the temperature of maximum intensities of characteristic peaks of COS was 270°C, of formaldehyde, formic acid, ethane and methanol 330°C, of SO_2, CO, acetic acid and ethylene 400°C, and of *p*-xylene and chlorobenzene 450–500°C (Figs 10–11).

At 10°C min^{-1} the temperature of maximum intensities of characteristic peaks of COS and methanol was 330°C, of CO and formic acid 400°C, of ethylene, formaldehyde and acetic acid 450°C and of SO_2, *p*-xylene, chlorobenzene and ethane 500–550°C the temperatures being shifted by 50–100°C towards higher temperatures as compared to these at the heating rate of 5°C min^{-1} (Figs 4 and 10–11).

During thermooxidation of Bulgarian coal and R12 samples at 5 and 10°C min^{-1} heating rates the emission of methane occurred mainly in one step with maximum intensity in FTIR spectra at 400–500°C, but at thermooxidation of U9 and R12 the emission of methane proceeded in two steps with maxima at 330 and 500–550°C (Fig. 12). At 50°C min^{-1} methane evolved in two steps with maxima in the FTIR spectra at 500 and 800°C. The intensive emission of methane at the beginning of the first step could be partially caused by methane adsorbed deeply in the pores of the samples.

At the heating rate of 50°C min^{-1} the emission of most of the gaseous compounds formed started at 250–300°C and of *p*-xylene and chlorobenzene at 350–400°C being shifted by 50–70°C towards higher temperatures as compared to lower heating rates (Fig. 5). The temperature of maximum intensities of characteristic peaks of COS and CO was 400°C, of methanol and ethane 600°C, of two ethylene peaks 450 and 700°C, of SO_2, *p*-xylene, acetic acid, formaldehyde and formic acid 800°C, and of chlorobenzene 900°C (Figs 5 and 10–11). So, the temperatures of maximum intensities of characteristic peaks were

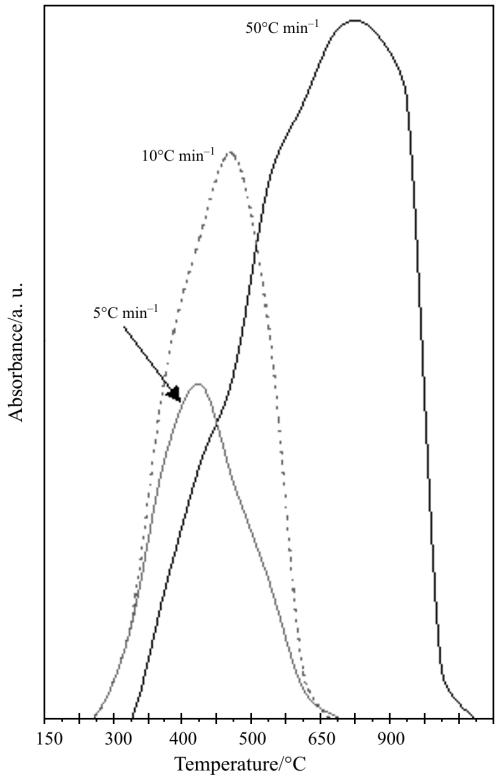

Fig. 10a Absorbance profiles of formaldehyde evolved at thermooxidation of Russian coal 12 at different heating rates

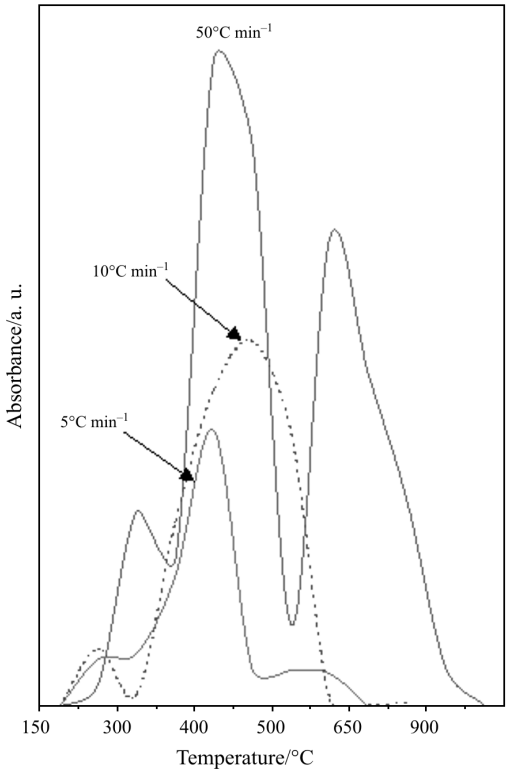

Fig. 11a Absorbance profiles of ethylene evolved at thermooxidation of Bulgarian coal 5 at different heating rates

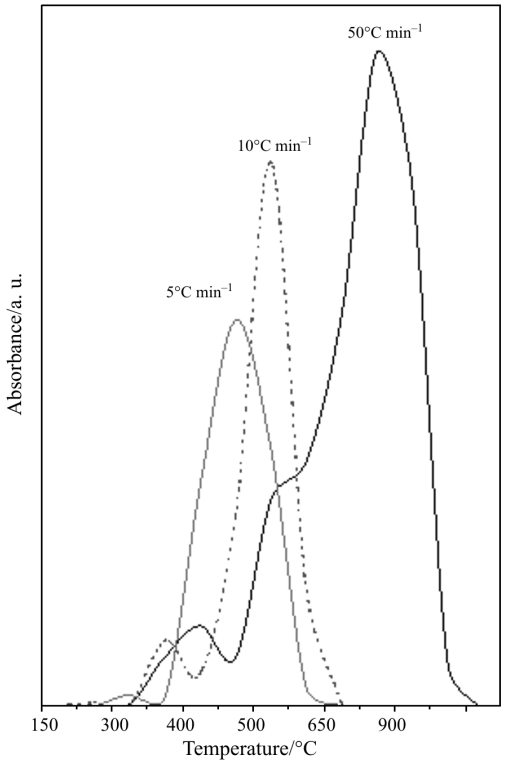

Fig. 10b Absorbance profiles of *p*-xylene evolved at thermooxidation of Russian coal 12 at different heating rates

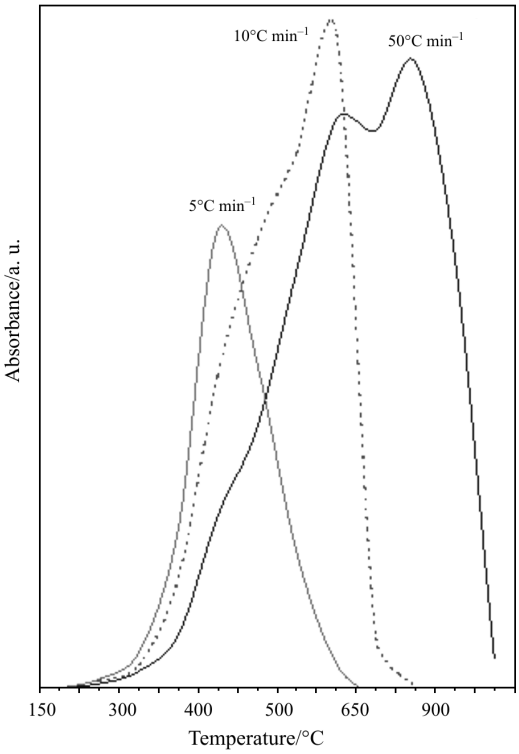

Fig. 11b Absorbance profiles of chlorobenzene evolved at thermooxidation of Bulgarian coal 5 at different heating rates

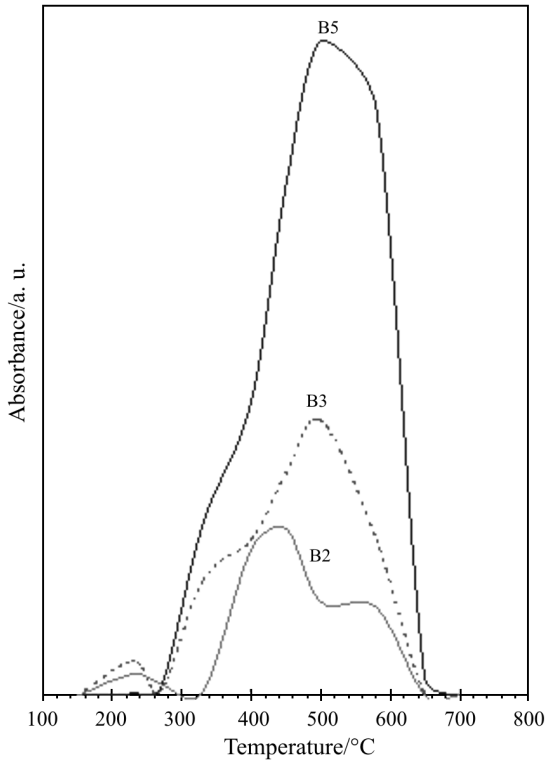

Fig. 12a Absorbance profiles of methane evolved at thermooxidation of Bulgarian coal samples at the heating rate of 10°C min^{-1}

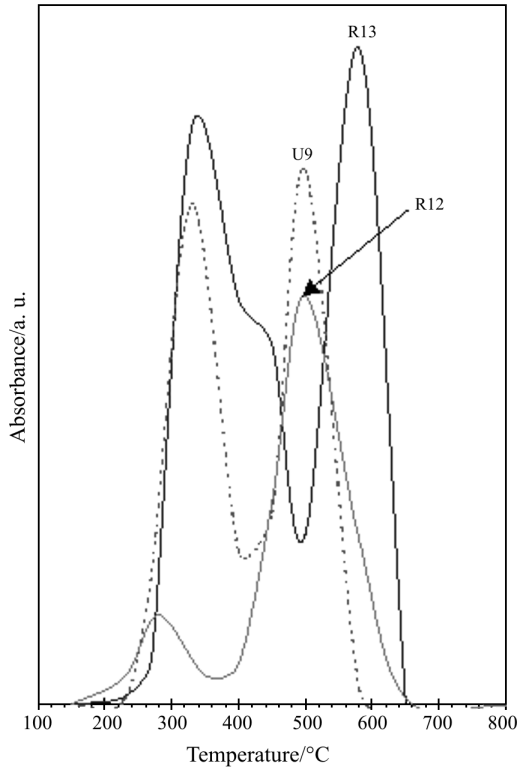

Fig. 12b Absorbance profiles of methane evolved at thermooxidation of Russian and Ukrainian coal samples at the heating rate of 10°C min^{-1}

shifted by 70–300°C and 150–450°C towards higher temperatures as compared to heating rates of 5 and 10°C min^{-1}, respectively.

Comparing the FTIR spectra obtained at different heating rates, differences were observed in the intensities of respective bands of gaseous species evolved. For most of the species like methane, ethylene, formaldehyde, formic acid, *p*-xylene, chlorobenzene the intensities of respective absorption bands increased together with the increase in the heating rate (Figs 10–11). It could be caused by the circumstance that at higher heating rates the contact-time between organic gaseous compounds formed at thermal treatment of coal samples and oxygen shortens and is not enough for the complete oxidation of these species before they leave the furnace.

Therefore, the results of FTIR analysis confirmed that there were no great differences in the individual species formed and emitted at thermooxidation of different coal samples studied, however, differences were observed in the intensities of characteristic absorption bands of species evolved and in the temperatures of peak maxima depending on the origin of the samples and the heating rate used.

Conclusions

The combined TG-FTIR study of thermal treatment of coal samples made it possible to identify a number of gaseous species formed and evolved as well as to determine the differences in the intensities of absorption bands of these species in FTIR spectra depending on chemical composition of the samples and on the heating rate used.

The formation and emission of CO_2, H_2O, CO, SO_2, NH_3, methane, ethylene, formic and acetic acid, formaldehyde, *p*-xylene and chlorobenzene was clearly identified in FTIR spectra of all the samples studied. The formation of COS, methanol, HCl, ethanol, ethane, acetaldehyde and possibly furan, at least on the level of traces, was also identified.

At the heating rate of 5°C min^{-1} the temperature of maximum intensities of the characteristic peaks of COS was 270°C, of formaldehyde, formic acid, ethane and methanol 330°C, of SO_2, CO, acetic acid, ethylene and *p*-xylene 400°C and of chlorobenzene 500°C. At 10 and 50°C min^{-1} these temperatures were shifted, respectively, by 70–300°C and 150–450°C towards higher temperatures and the respective absorption bands in FTIR spectra were, as a rule, more intensive.

A good correlation between the thermal behavior and the elemental composition of organic matter of different samples was observed.

Acknowledgements

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References

1 R. M. Carangelo, P. R. Solomon and D. J. Gerson, Fuel, 66 (1987) 960.
2 A. Zanier, J. Therm. Anal. Cal., 56 (1999) 1389.
3 V. Strezov, J. A. Lucas, T. J. Evans and L. Strezov, J. Therm. Anal. Cal., 78 (2004) 385.
4 I. Pitkänen, J. Huttunen, H. Halttunen and R. Vesterinen, J. Therm. Anal. Cal., 56 (1999) 1253.
5 R. Lu, S. Purushotama, X. Yang, J. Hyatt, W-P. Pan, J. T. Riley and W. G. Lloyd, Fuel Process. Technol., 59 (1999) 35.
6 T. Kaljuvee, J. Pelt and M. Radin, J. Therm. Anal. Cal., 78 (2004) 399.
7 M. V. Kök and M. R. Pamir, J. Anal. Appl. Pyrolysis, 55 (2000) 185.
8 F. Jorgensen and F. Moyle, J. Thermal Anal., 25 (1982) 473.
9 Y. Pelovski and V. Petkova, J. Therm. Anal. Cal., 56 (1999) 95.
10 M. V. Kök and M. R. Pamir, J. Therm. Anal. Cal., 53 (1998) 567.

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